PROGRESS REPORT I

(March 1983 - May 1983)

De-icing and Prevention of Ice Formation of/on

Offshore Oil-Drilling Platforms

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PROGRESS REPORT I

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by

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The objective of this research is the development of efficient de-icing methods for prevention of ice formation of/on oil drilling platforms located off-shore in cold ocean regions.

Coatings are investigated first.

The requirements for such a coating are:

(1) About 90% or more reduction of adhesive strength of the ice/coating interface.

(2) Sufficient adhesive strength of the coat to the substrate.

(3) Resistance to cracking or peeling of the coating due to impacts by sea spray and waves.

(4) Resistance of coating to other environmental deterioration, particularly to near u.v. light radiation of the sun.

(5) Easy application of coating to substrate. The block-co-polymer LR5630 (polysiloxane and polycarbonate) manifested was investigated first because of its

superior properties for de-icing of lockwalls.[1]) This co-polymer contained 65% w/w polysiloxane, T_g -66°C.

Point (3) above; i.e. mechanical-rheological properties and hardness of coating of LR5630 was investigated first.

A tensile (strength) apparatus was designed and made in our workshop (see Fig. 1). Hardness measurements were preliminarily carried out by the pencil hardness method. Coating compositions were varied by trying to crosslink the polydemethyl-siloxane component or by using double layers (i.e., undercoats). The experimental part of this work is described below.

(A) Tensile Apparatus

Fig. 1 shows a schematic drawing of the tensile apparatus: (1) sample between chucks; always 1 cm, (2) micrometer screw for making contact between the elastic piece of spring (5) and the lever (3a), of the Statham strain gauge (3).

The sample is held between the pulley and spring by nylon fish line. The strain rate is 2.9 mm/s, but will be made changeable in the future. The dimensions on the samples are: length, ℓ_o, between chucks 1.0 cm, width 0.5 cm (these dimensions remain constant); thickness is measured for each sample (ca. 50-100 μ.); testing temperature 20-21°C.

Fig. 2 gives a magnified view of the sample held by the chucks; it is self-explanatory.

For such a sample (i.e. LR5630) Young's (tensile) modulus can be calculated from the initial slope of the stress-strain curve. The result is 9 kg/cm^2 (8.8 x 10^6 dyne/cm^2, 9 x 10^5 Pa/cm^2).

Leverne-Williams et al.[2]) measured rheological properties of the same block-co-polymer at a strain rate of 0.3 mm/s. From his small graph the tensile modulus can be derived as about 11 kg/cm^2. Tensile strength and modulus will be discussed in the next report.

It was ascertained that Young's modulus obtained from the slope of the linear parts of our strain vs. stress curves are quite similar to the one obtained by Leverne-Williams[2] for the same block-polymer. Numerical results will be discussed in more detail in Progress Report II when further numerical results will be available.

This indicates that the tensile apparatus functions satisfactorily for our purpose. A preliminary experimental result is given below.

Young's (i.e. tensile) Modulus of LR5630

	Present Work	Leverne-Williams[2]
Young's Modulus	9.1 x kg/cm^2	11 kg/cm^2
Strain rate	2.9 mm/s	0.3 mm/s (2 cm/mm)
Dimension of Sample:		
Width	5 mm	–
Span Between Chucks i.e. Length	10 mm	–
Thickness	ca. 50 μ – 100 μ	–
Temperature	20°C – 21°C	23°C

Some preliminary results are given below:

(B) Various Preliminary Results Using Polydimethylsiloxane-polycarbonates Block-Co-Polymers

(1) LR5630: Film thickness 0.18 mm; film width 0.5 cm, distance between chucks 1.1 cm. The break occurred at one of the chucks:

Tensile strength 23 kg/cm^2 (ca. 22°C); elongation at break was not measured.

(2)   LR5630:   Film thickness 0.050 mm, width 0.6 cm,   chucks 0.7 cm.

Tensile strength 38 kg/cm^2, elongation at break 974%,

22°C; strain rate 2.9 mm/s;   (sensitivity of Sanborn recorder: 3.6 $\pm$ 0.1 mm/g.)

A thickness of ca. 0.050 mm was found to be preferable over thicker films.

(C)   Hardness of Coatings

We know from previous work that LR5630 was the best abhesive polymer for de-icing lockwalls. We also know that the abhesive force does not vary for such a coating when kept under water for various time periods.

A stock solution of LR5630 was prepared having a composition as follows:

LR5630	4.0 g
Silicone Oil (Thomas No. 6407)	0.4 g
Toluene	20.0 ml

A coat was made on a surface - oxidized (rusty) iron plate (3" x 3"). The dried film had a thickness of 0.15 to 0.2 mm.

A jet of saline water (3.5% w/v NeCl) was directed onto this coat. The jet nozzle had a diameter of 5.4 mm. The jet was kept on for 2.5 h. The volume exit rate was 800 ml/s and the linear rate 3.9 m/s. The film resisted this treatment without damage.

However under actual conditions, the impact of waves and spray are about 10 times stronger; ice particles and possibly other particles are contained in sea water sprays.

Hence experiments were carried out dropping a sphere (18.6) inside a glass tube on a one mm thick film coated on a rough iron plate. The velocity at impact was 313 cm/s and the kinetic energy 9.1×10^6 erg. It was apparent that around the indentation of the film especially at rought spots of the substrate surface, the

coating was damaged.

Hence, the next step of the work consisted in trying to make this coating harder without altering appreciably the ice/coating adhesive strength.

First, crosslinking of the polysiloxane-blocks was attempted; benzoyl-peroxide (BzO_2) was used as the crosslinking agent. 2.5% w/w BzO_2 was added to the above stock solution. A coat was spread on an Al-plate. This was heated to 125°C for 0.5 h, 1.0 h and 2.0 h, respectively. Adhesion to the Al-plate improved with time of heating. However, the film remained soluble in toluene and the hardness of the film remained the same. Thus, crosslinking was not achieved in this case.

Next, siloxane, high gum (Polysciences, Inc.) was dissolved in the stock solution, 5% w/w of BzO_2 was added. The coating was heated similarly as before. Still, crosslinking did not occur. Here, the stickiness of the coating decreased on heating.

The block-polymer XD-11 (25% w/w polysiloxane; T_g 100°C) which is harder than LR5630 was tested. Its stock-solution composition was as follows:

XD-11	1.5 g
Toluene	5.0 ml
CH_2Cl_2	10.0 ml

Coats were prepared on glass-plates with increasing amounts of silicone oil (Thomas): 0.5 ml up to 0.75 ml on addition of 0.9 ml silicone oil, polymer and oil separated.

The hardness of the XD-11 films was also tested by the pencil hardness method. Even the softest pencil (6B) penetrated the film (thickness ca. 10 μ). Adhesion of the film to glass decreased with increasing silicone oil content.

Also, polysiloxane gum was tested. Up to 40% of the gum was added to the XD-11 films. But again, all films were penetrated by the pencil (6B).

The next experiments dealt with double coats of Butvar B-90 and LR5630. It had been found during previous work (lockwalls) that LR5630 is improved in its mechanical properties by a Butvar primer (probably also mutual diffusion takes place to a certain extent). Previously, it proved to be the best double coat system.

The stock solution for Butvar B-90 was as follows:

Butvar B-90	1.5 g
Toluene	10.0 ml
Ethanol	8.0 ml

Coats were made on glass plates and dried at room temperature for one day. Even the hardest pencil (H-6) did not damage this coat.

Such double coatings are being further investigated.

Summary (Abstract):

Preliminary experiments have been carried out.

(1) A tensile apparatus was designed and built which proved to be satisfactory.

(2) Experiments showed that the polysiloxane-polycarbonate block-co-polymer proved to be too soft to withstand impacts of waves and sea spray as expected under actual conditions.

(3) Crosslinking of the siloxane component in the block-co-polymer by benzoylperoxide was not achieved.

(4) The hardness of films of the block-co-polymer, XD-11, even when modified by additions, was also not sufficiently resistant.

(5) Double coats of Butvar-B-90 (Primer) and LR5630 appeared to be sufficiently hard. These systems are being further investigated.

References

(1) H.H.G. Jellinek, H. Kachi, S. Kittaka, N. Lee and R. Yokoth, Ice Releasing Block-
     Co-Polymer Coatings, Coll. Polym. Sci. <u>258</u>, 544-551 (1978).

(2) W. Maung, K. M. Chua, T. H. NG and H. Leverne-Willaims, Dynamic Mechanical
     and Thermomechanical Properties of Silicone-polycarbonate Block-Co-Polymers, Pol.
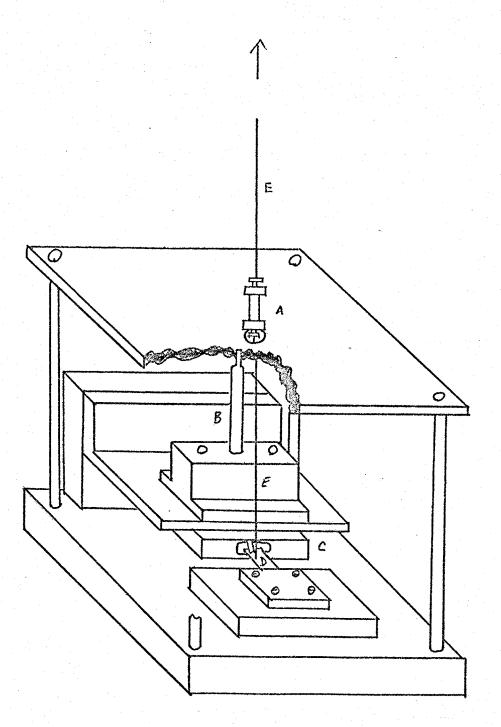   Enc. Sci., <u>23</u>, 439-445 (1983).

FIGURE 1:   Tensile Tester

A: Sample Holder

B: Micrometer screw for moving the transduce

C: Transducer (Statham Transducers, Inc.
     Model G10B-0.3-350)

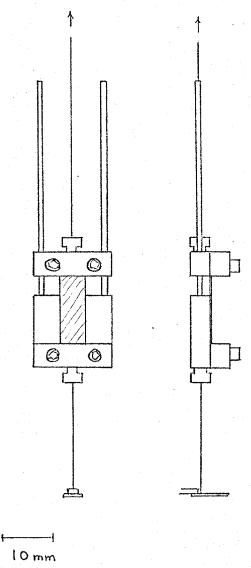D: Stainless steel spring

E: Nylon thread (475μ diameter)

10 mm

Fig. 2

PROGRESS REPORT II

(June 1983 - August 31, 1983)

De-icing and Prevention of Ice Formation of/on

Offshore Oil-Drilling Platforms

Grantor: U. S. Army Corps of Engineers, CRREL
Hanover, New Hampshire 03755

Grantee: Clarkson College of Technology
Potsdam, New York 13676

Grant No.: DACA 89-83-0003

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The work on strength of films with a variety of added compounds has been carried

on with the tensile strength apparatus described in Progress Report I. In addition,

some shear abhesion and erosion tests by impact of a water jet were performed.

I. Tensile Strength Experiments.

Young's modulus of sample LR5630.

Parameters for these tests were given in Progress Report I, p. 3.

2 g of the biscarbonate-siloxane co-polymer LR5630 were dissolved in a

mixture of 4.0 ml toluene plus 4.0 ml methylene dichloride (CH_2Cl_2). Certain amounts

of silicone oil were added to such solutions (H. Thomas 6428-R15). The oil is not

completely miscible and the solution became increasingly more milky as additional

amounts of silicone oil were added. Films were cast from such mixtures and the

film surfaces were progressively more oily as with increasing silicone oil content,

noticeably so beyond a mixing ratio of LR5630 : silicone oil = 100/60 w/v. a 1:1

mixture of LR5630 to silicone oil separated out.

Films were cast on glass-slides and spread with a knife-like coater. The films were dried not longer than two days at room temperature. A film sample for tensile tests could be easily obtained by peeling the film off the slide. The range of film thickness was about 50 to 100 μm. The temperature was controlled to ± 1°C. Each tensile value in Table I represents the average of about 10 tests.

TABLE I

Young's (Tensile) Modulus of

LR5630 Films Plus Various Amounts of Silicone Oil

(See also Fig. 1)

Temp. °C	(Young's) Tensile Modulus, $E(kg/cm^2)$					
	LR5630/Silicone Oil					
	100/0	100/10	100/20	100/40	100/60	100/80
20	9.8 ± 0.5	8.3 ± 0.7	6.1 ± 1.0	5.7 ± 0.7	5.5 ± 0.6	4.3 ± 0.3
10	13.5 ± 1.3	11.8 ± 1.8	10.5 ± 1.3	7.9 ± 1.7	7.3 ± 0.7	6.7 ± 1.4
0	19.6 ± 3.6	15.9 ± 0.9	12.1 ± 1.1	11.5 ± 1.5	9.1 ± 1.3	7.8 ± 1.6
-10	24.1 ± 3.4	19.4 ± 3.8	18.2 ± 4.8	12.3 ± 2.8	10.4 ± 3.1	8.9 ± 3.9
-20	30.6 ± 4.0	24.1 ± 9.3	21.5 ± 2.9	16.5 ± 4.3	12.1 ± 3.3	10.4 ± 1.2

The results can be formally represented by an Arrhenius type energy of activation plotting $\log_{10}$ (tensile modulus) vs. the reciprocal absolute temperature (E ~ Young's Modulus)

$$lg_{10} \, E = \frac{E_{Arrh}}{2.303 \, RT} \quad \log A$$

E_{Arrh} is the apparent Arrhenius energy of activation, 'A' the pre-exponential factor and R the ideal gas constant.

All values for 20°C showed systematic lower deviations from the respective straight line; they were not included in the evaluation of the energy of activation. The reason for this is not understood at present (See Fig. 2). It is possible that at +20°C, the co-polymer starts to enter an elastomeric range.

TABLE II

(Formal) Apparent Energies of Activation

for Young's Modulus

(See Figs. 2 and 3)

LR5630/Silicone Oil (w/v)	E_{Arrh}(kcal/mol)
100/0	4.2
100/10	3.7
100/20	3.4
100/40	2.8
100/60	2.7
100/80	2.3

These energies of activation also indicate increased mobility with increasing oil content.

II. Abhesion Tests

The apparatus and procedure were the same as used in previous work [See H.H.G. Jellinek, H. Kachi, S. Kittaka, M. Lee and R. Yokota, Colloid and Polym. Sci., 256, 544-551, (1978)].

TABLE III

Adhesive Strength of LR5630

Plus Silicone Oil

LR5630/Silicone Oil (w/v)	Adhesive Strength kg/cm^2	No. of Tests
(1) 100/20 1g LR5630 : 10.0 ml Toluene: 0.2 ml oil	0.045 ± 0.003	5
(2) 100/0 3.5g LR5630 : 15 ml Toluene: -	0.61 ± 0.14	5
(3) 3.5g LR5630 : 15.0 ml Toluene plus Tullanox #500 An Al-plate was coated with LR5630 film and dried; it was immersed in #500 Tullanox powder for one minute and brushed off. Film thickness 60-70 μm.	0.97 ± 0.71	5

Tullanox (formerly Silanox) is a silica powder made hydrophobic by a surface layer of silanes. The hydrophobic CH_3-groups "stick" out from the surface of the particles. "Tullanox" has a so-called "super-hydrophobic" repellency of water. Tullanox #500 has a particle size of about 70 $\overset{o}{A}$ = 7 x 10^{-7}cm, hence it has a very large specific surface area. The contact angle of water is extraordinarily large (θ = 138°). This is due to its hydrophobicity and surface roughness. A monolayer of Tullanox #500 consists of about 2 x 10^{12} particles/cm^2. Such a surface is relatively rough and therefore holds a drop of water slightly above the coated surface. An effect is produced which is similar to water-shedding surfaces found in nature (insects, foliage). A sheen or so-called "gaseous plastron" effect is observed on immersion in water.

The roughness explains the increased adhesive strength of films with Tullanox measured by shear. The hydrophobicity is certainly very high as a drop of water shows a contact angle above 90°C. Thus it appears that adhesive strength measurements will have to be modified to some kind of peeling procedure.

A number of additional abhesion tests were performed with Tullanox #500 added.

TABLE IV

Adhesive Strength of LR5630

Plus Tullanox #500

	Adhesive Strength	No. of Tests
(4) LR5630 LR5630 1.0g; 2.5 ml Toluene; 2.5 CH_2Cl_2	0.30 $\pm$ 0.18	5
(5) LR5630; brush coating of #500; otherwise, same composition as (4).	2.41 $\pm$ 0.37	5
(6) LR5630; #500 applied by knife-like coater; otherwise, same composition as (4). 0.5g Tullanox suspension in 10.0 ml Toluene.	0.92 $\pm$ 0.23	5
(7) LR5630; #500 milled into mixture. ball-milled solution; PR5630 563 or 1.0g, toluene 10.0 ml, #500 0.6g. (milled for 11 h)	0.58	1

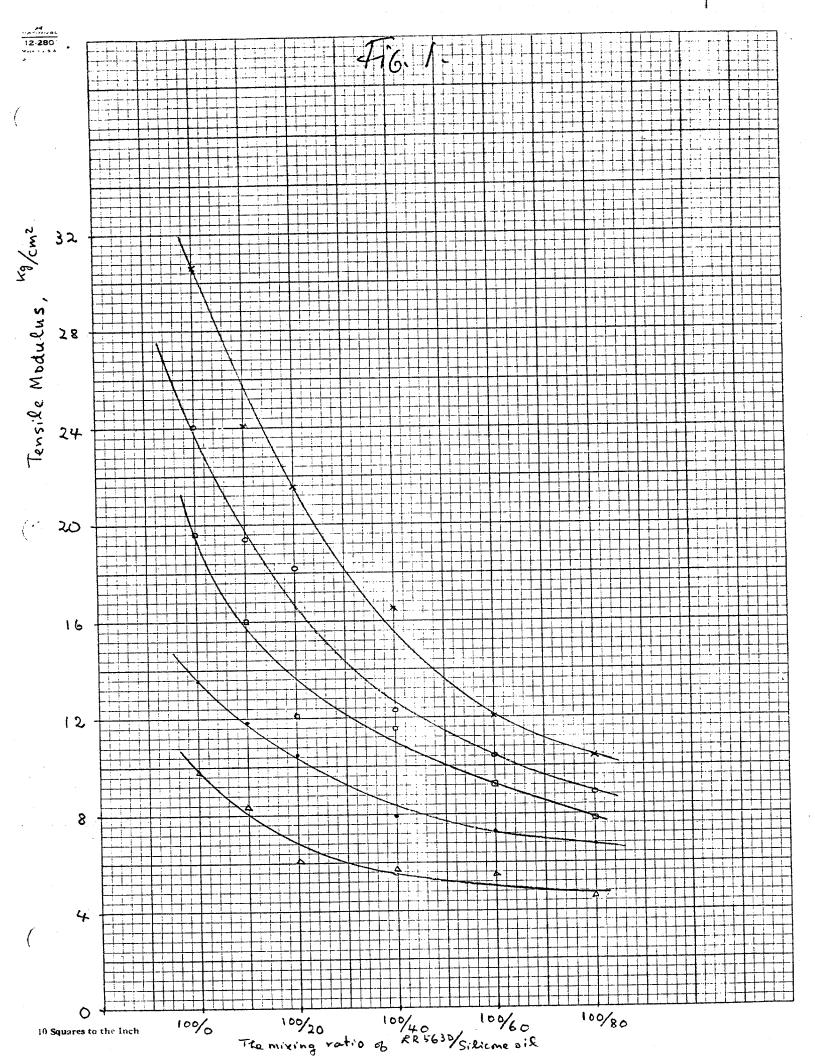Contact angles of water with (5) and (6) were > 90° and also larger than for #(4) and #(7).

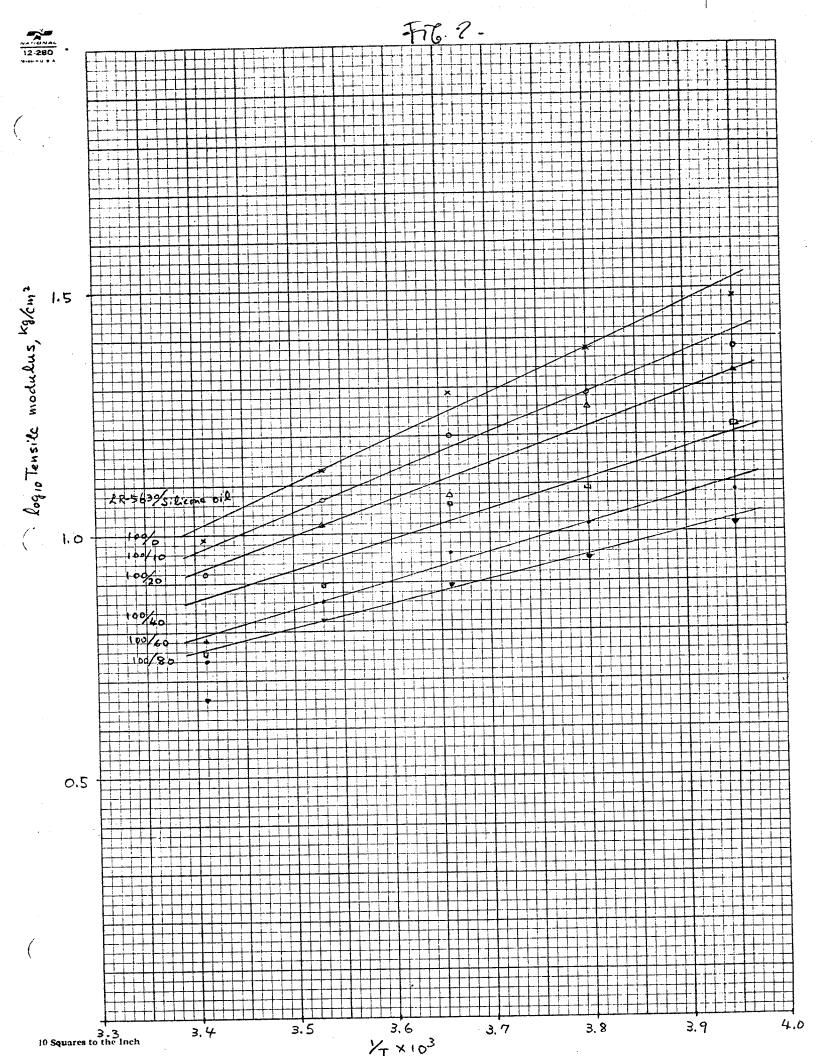The types of experiments described above will be continued with many variations.
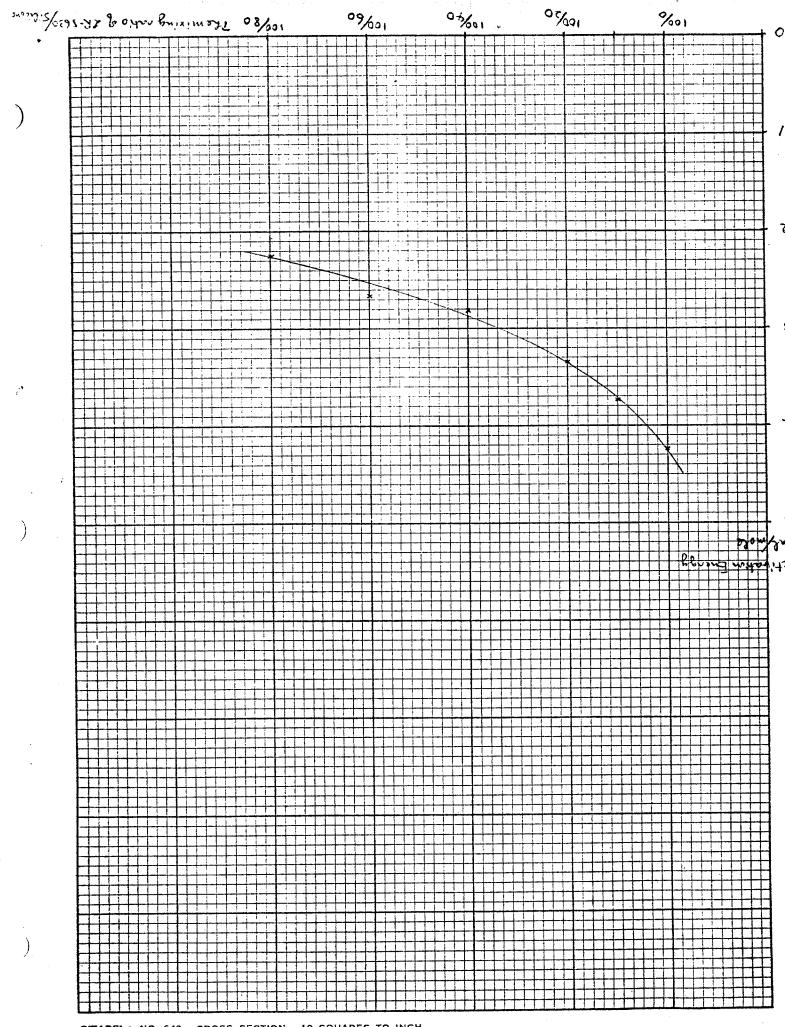
III. Erosion of LR5630 Films

A coat of LR5630, ca 0.15 mm thick containing 10% by volume of silicone oil was cast on a rusty iron plate   (7.5 cm x 7.5 cm). A jet stream of water was directed on to the coat having a linear velocity of ca. 14 m/s. The diameter of the nozzle was 0.3 cm and the volume rate 100 ml/s. The film was only slightly damaged.

According to information received from CRREL, the wind velocity hitting an oil drilling system will be in the range of 40-70 mi/h (24 m/s). We estimate that our water jet has a larger impact than such a wind.

It is our intention to send plates to CRREL with various coats for exposure to the actual environment in order to obtain an estimate as to the resistance of such coats under actual service conditions.

Fig. 1

The mixing ratio of RR 5630/Silicone oil

FIG. 2.

$\log_{10}$ Tensile modulus, kg/cm^2

$1/T \times 10^3$

LR-5630/Silicone oil

100/0
100/10
100/20
100/40
100/60
100/80

10 Squares to the Inch

Fracture Energy
in/mole(?)